Superconductivity at 32K and anisotropy in $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$ crystals

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Single crystals of $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$ are successfully grown with the superconducting transition temperatures ${T_c}^{onset}$=32K and ${T_c}^{zero}$=31.4K. The Hall coefficient exhibits a multi-band behavior, which is very similar to that of all other Fe-based superconductors. We found that the susceptibility at the normal state decreases with decreasing the temperature, indicating a strong antiferromagnetic (AFM) spin fluctuation at the normal state, which might be related to the superconductivity (SC). We also determined the upper critical fields in *ab*-plane and along *c*-axis. The anisotropy of the superconductivity determined by the ratio of ${H_{c2}}^{ab}$ and ${H_{c2}}^{c}$ is estimated to 5.0, which is larger than that in (Ba,K)Fe_2As_2 and $BaFe_{2-x}Co_xAs_2$, but smaller than that in cuprate superconductors.

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Since superconductivity at 26K in $LaO_{1-x}F_xFeAs$ was discovered by Kamihara *et al.*[1], the iron-based superconductors have received worldwide attention in the last three years. There have been four major types of iron-based compounds reported to exhibit SC after doping or under high pressures, i.e. 1111-type ReFeAsO (Re = rare earth)[1–6], 122-type BFe_2As_2 (B=Ba, Sr or Ca)[7–9], 111-type AFeAs (A = alkali metal)[10], and 11-type tetragonal $FeTe_{1-x}Se(S)_x$[11, 12]. All these iron-based superconductors share a common layered structure based on a square planar Fe^{2+} layer, tetrahedrally coordinated pnictogen (P, As) or chalcogen (S, Se, Te) anions. The emergence of superconductivity upon destruction of long-range antiferromagnetic (AFM) order is qualitatively similar to observations in the layered cuprate high temperature superconductors. However, in the cuprates, the repulsive interaction among the electrons is so strong that the parent compounds are Mott insulators. By contrast, all iron-based parents above mentioned are metallic.

Very recently, superconductivity at about 30K was reported in $K_xFe_2Se_2$ [13] and $Cs_{0.8}Fe_2Se_{1.96}$ [14]. Our group [15] have confirmed that superconductivity at 31K occurring in the newly (Tl,K)Fe_xSe_2 compound (denoted as 122-type iron-chalcogenide) is also in proximity of an AFM insulator. We found that (Tl,K)$Fe_{1.5}Se_2$ with a Fe-vacancy super-lattice is an AFM insulator with the Neel temperature, T_N=250 K, which can be regarded as the parent of this system. With increasing the Fe-content, the AFM order is reduced. When the magnetism is eliminated, superconductivity at 31K emerges. In this letter, we report the successful growing of the single crystals for another new compound $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$. The onset and zero-resistivity transition temperature were estimated to be 32 K and 31.4 K, respectively. We found that the Hall coefficient exhibits a multi-band behavior. The susceptibility result indicates a strong AFM spin fluctuation at the normal state. We also determined the upper critical fields in *ab*-plane and along*c*-axis. The anisotropy of the superconductivity determined by the ratio of ${H_{c2}}^{ab}$ and ${H_{c2}}^{c}$ is estimated to be 5.0.

Single crystals were grown by the Bridgeman method. First, Rb_2Se, Tl_2Se, Fe and Se powders with high purity (99.99%) were mixed in an appropriate stoichiometry and were put into alumina crucibles and sealed in evacuated silica tube. The mixture was heated up to 950^{o}C and held for 6 hours. Then the melting mixture was cooled down to 700^{o}C in the cooling rate of 3^{o}C/h and finally the furnace was cooled to room temperature with the power shut off. The obtained single crystals show the flat shiny surface and are easy to cleave. The composition of crystals, $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$, was determined by using an Energy Dispersive X-ray Spectrometer (EDXS). The structure of single crystals was characterized by X-ray diffraction (XRD). Magnetic susceptibility measurements were carried out using the *Quantum Design* MPMS-SQUID. The measurements of resistivity, Hall effect and magneto-resistance were done using the *Quantum Design* Physical Properties Measurement System PPMS-9.

Figure 1 shows the XRD (Fig.1a) pattern of powder obtained by grounding the crystals and single crystal XRD (Fig.1b) pattern for $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$. Most peaks in the powder XRD pattern can be well indexed with a $ThCr_2Si_2$-type structure (space group: $I4/mmm$). The lattice parameters, $a = 3.896$Å, and $c = 14.303$Å was obtained by the fitting XRD data. One small peak marked by a triangle belongs to FeSe compound due to small amount existing between crystals. Only $(00l)$ peaks were observed in the single crystal XRD pattern, indicating that the crystallographic c axis is perpendicular to the plane of the single crystal. The interesting is that there is another series of $(00l)$ peaks (marked by the asterisks) with $c = 14.806$Å, which is larger than that of the main phase, implying that there may be a modulation structure along c axis due to the existence of Fe-vacancy. But there is only a small peak appearing in the powder XRD

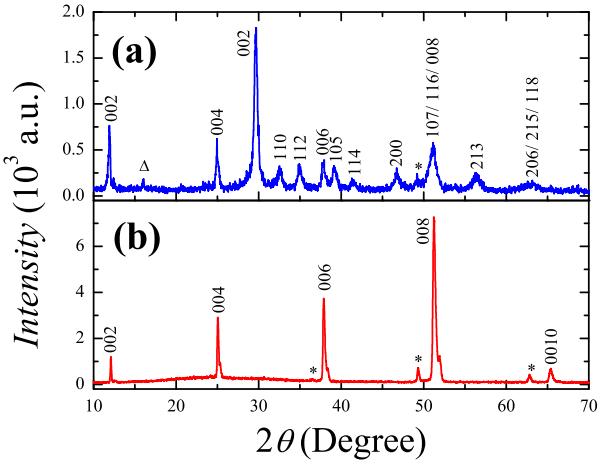

FIG. 1: (Color online)(a) Powder and (b) Single crystal X-ray diffraction pattern of $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$

pattern. This modulation structure was also observed in $Cs_xFe_2Se_2$ crystals[14].

Figure 2(a) shows the resistivity in *ab*-plane, ρ_{ab}(T), and along *c* axis, ρ_c(T), as a function of temperature for $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$ crystal. At higher temperatures, both ρ_{ab}(T) and ρ_c(T) exhibit a semiconductor-like behavior, and displays a maximum resistivity at about 150 K, and shows a metallic behavior below 150 K. A metal-insulator transition occurs at about 150K. Similar behavior of ρ_{ab}(T) was also observed in $K_xFe_2Se_2$ [13], $Cs_xFe_2Se_2$ [14], (Tl,K)Fe_xSe_2[15] and $Rb_xFe_2Se_2$ [17, 18] crystals. We identified that the temperature of the maximum resistivity in ρ_{ab}(T) depends on the actual Fe-content in the crystals for the similar system (Tl,K)Fe_xSe_2 [15]. It should be noted that the absolute value of resistivity at the normal state is quite large, for example, ρ_{ab} is of 10 mΩ cm at 300 K, which is much larger than that in other typical iron-based superconductors. This may be attributed to the this compound residing in the under-doping region in the phase diagram, as discussed in (Tl,K)Fe_xSe_2 system by us.[15] Another, from the ratio value of ρ_c/ρ_{ab}=30-45 estimated from the resistivity data at the normal state, the anisotropy is smaller than that in (Tl,K)Fe_xSe_2 system, where ρ_c/ρ_{ab}=70-80 [15].

In order to explore the electronic structure in this compound, we measured the Hall coefficient R_H. Figure 2(b) shows the temperature dependence of Hall coefficient, R_H(T), for$Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$ crystal. The interesting is that the change in the signal of R_H(T) at 214 K occurs from positive to negative, which is the typical behavior of the multi-band of the electronic band and a common feature of Fe-based superconductors. Above 214K, the positive value of R_H implies that the carrier in this compound is dominated by holes. The negative value of R_H from 214K to T_c indicates that the carrier in the compound is dominated by electrons. This result means that

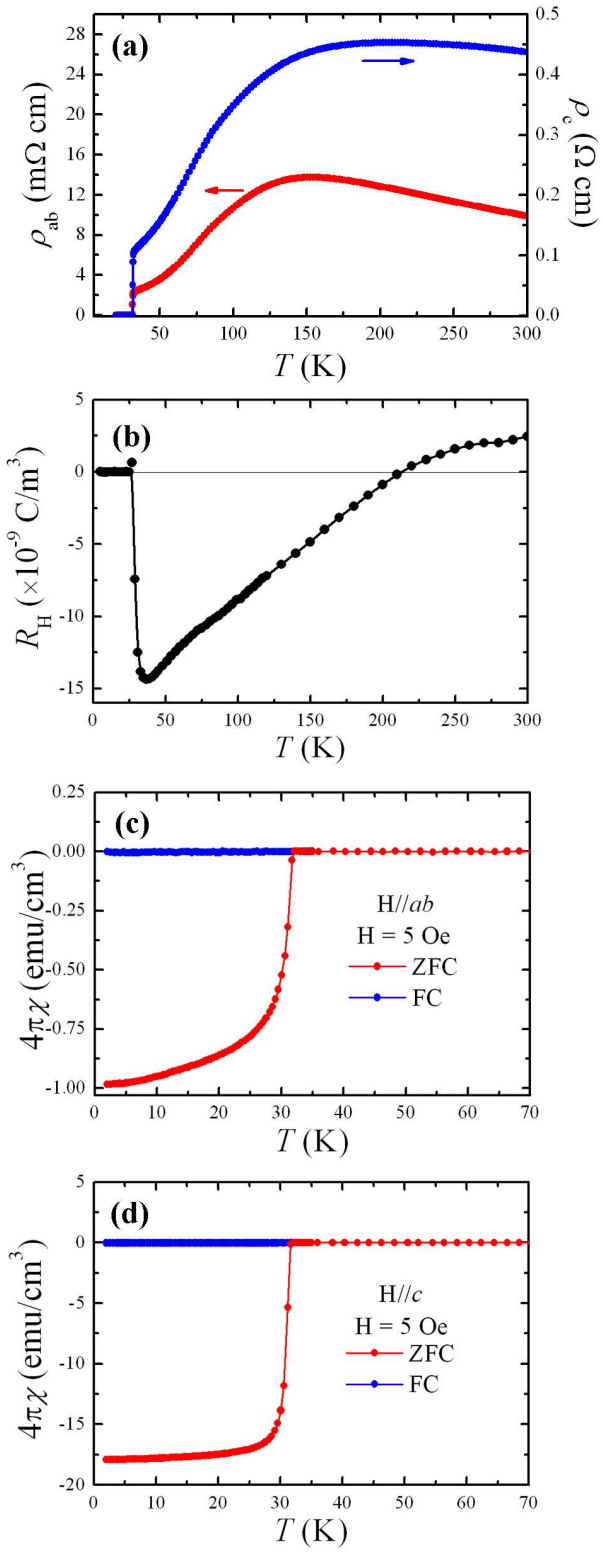

FIG. 2: (Color online)(a) Temperature dependence of *ab*-plane and *c*-axis resistivity. (b)Temperature dependence of Hall coefficient. (c) Temperature dependence of dc magnetic susceptibility for both zero field cooling (ZFC) and field cooling processes (FC) at a magnetic field of H= 5 Oe applied along c axis and (d) in *ab*-plane for $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$ crystal.

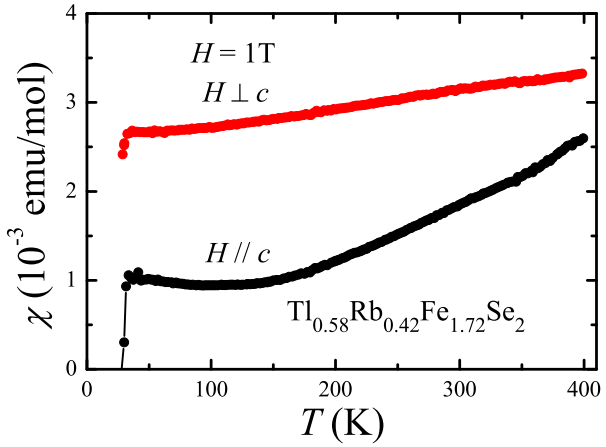

FIG. 3: (Color online) The magnetic susceptibility measured at 1 Tesla for $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$ crystal with the magnetic field along and perpendicular to c-axis.

there are both hole pocket and electron pocket near the Fermi energy, which is very similar to that of all other Fe-based superconductors although there are Fe vacancies on the Fe-planar in $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$ compound. In the (Tl,K)Fe_xSe_2 system [15], we found that no signal change of R_H occurs, indicating that the carrier is dominated by electrons from T_c to 350 K. The difference of the electron structure between both may be due to the difference between K and Rb radii.

From both ρ_{ab}(T) and ρ_c(T), we can see that a sharp superconducting transition occurs at $T_c{}^{onset}$=32 K, $T_c{}^{mid}$=31.5 K and $T_c{}^{zero}$=31.4 K , confirmed by the existence of diamagnetism below T_c (see Fig. 2c and 2d). As the magnetic field is applied in c axis, the diamagnetic signal at the superconducting state is very large and over negative unity due to larger demagnetization factor. When the magnetic field is applied in ab plane, the demagnetization effect can being ignored, diamagnetic signal reaches to 98% at low temperatures. All of these demonstrate a bulk SC emerging in the $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$ crystal, which is different than that observed in (Tl,K)Fe_xSe_2 by us [15], where no bulk SC was observed in the range of $1.70 \leq x < 1.78$.

Figure 3 shows the magnetic susceptibility at the normal state as a function of temperature, χ_c(T) and χ_{ab}(T), for the $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$ crystal with a magnetic field of 1 T applied parallel and perpendicular to the c-axis. A drop in susceptibility at about 30 K corresponds to the superconducting transition. When the magnetic field was applied along c-axis, the susceptibility, χ_c(T) value above 150 K decreases linearly with decreasing the temperature, then shows a little increase until the superconducting transition occurs. When the magnetic field was applied in ab-plane, the χ_{ab} value decreases well linearly with decreasing the temperature in the temperature range of 30K $\leq$ T $\leq$ 400K. The behavior of both χ_{ab} and

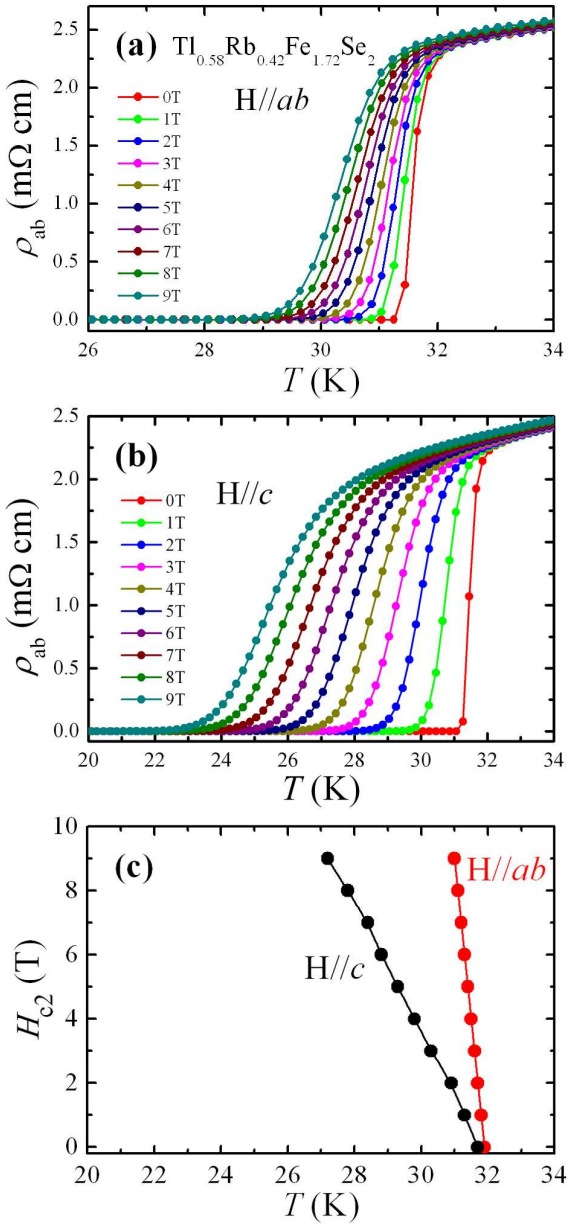

FIG. 4: (Color online) The temperature dependence of the resistivity with magnetic field (a) parallel and (b) perpendicular to the ab-plane, respectively. (c) The temperature dependence of upper critical field H_{c2}(T) for $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$ crystal

χ_c drop with decreasing the temperature implies a strong AFM spin fluctuation at the normal state, which might be related to the SC.

The temperature dependence of resistivity from 20K to 34K with different magnetic fields applied along c-axis and in ab-plane is shown in Fig. 4(a) and 4(b). We defined the T_c as the temperature where the resistivity was 90% drop at the superconducting transition to determine the upper critical fields, H_{c2}. The

$H_{c2}(T)$ determined in this way is shown in Fig. 4(c). The $H_{c2}(T)$ exhibits a rather linear temperature dependence for both directions. Thus we can easily get the value of the slope for both directions: $-dH_{c2}{}^{ab}/dT|_{T_c}$ =10.0 T/K , $-dH_{c2}{}^{c}/dT|_{T_c}$ =2.0 T/K. The $H_{c2}(0)$ value can be estimated by the Werthamer-Helfand-Hohenberg (WHH) equation [16] $H_{c2}(T)$=0.693[-(dH_{c2}/dT)]T_c with T_c=32 K, to be 221 T and 44.2 T with the magnetic field applied in ab-plane and along c-axis, respectively. The anisotropy $H_{c2}{}^{ab}(0)/ H_{c2}{}^{c}(0)$ is about 5.0, which is larger than that in $Ba_{0.6}K_{0.4}Fe_2As_2$[20] and $Ba(Fe_{0.92}Co_{0.08})_2As_2$ [21].

In summary, we successfully grew the single crystals of $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$ with the superconducting transition temperature $T_c{}^{onset}$=32 K and $T_c{}^{zero}$=31.4 K. The Hall coefficient exhibits a multi-band behavior, which is very similar to that of all other Fe-based superconductors although there are Fe vacancies on the Fe-planar in $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$ compound. We also determined the upper critical fields in ab-plane and along c-axis. The anisotropy of the superconductivity determined by the ratio of $H_{c2}{}^{ab}$ and $H_{c2}{}^{c}$ is estimated to 5.0, which is larger than that in $Ba_{0.6}K_{0.4}Fe_2As_2$ and $BaFe_{1.92}Co_{0.08}As_2$, but smaller than that in cuprate superconductors.

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